PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Form PCT/IPEA/416
International application No. PCT/CZ2004/000049	International filing date *(day/month/year)* 23.08.2004	Priority date *(day/month/year)* 01.09.2003

International Patent Classification (IPC) or national classification and IPC
C07C29/62, C07C31/36

Applicant
SPOLEK PRO CHEMICKOU A HUNTI VYROBU, AKCIOVA ...

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 7 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *sent to the applicant and to the International Bureau)* a total of 3 sheets, as follows:
      ☒ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      ☒ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

☒	Box No. I	Basis of the opinion
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the international application
☒	Box No. VIII	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
27.06.2005	16.11.2005

Name and mailing address of the international preliminary examining authority:
European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4465

Authorized Officer
Grammenoudi, S
Telephone No. +49 89 2399-8324

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/CZ2004/000049

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

   ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3 and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4)
   - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

   Description, Pages

   1-8 as originally filed

   Claims, Numbers

   1-16 filed with telefax on 27.06.2005

   ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

4. ☒ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
   - ☐ the description, pages
   - ☒ the claims, Nos. 12-16
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

* *If item 4 applies, some or all of these sheets may be marked "superseded."*

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-11,16
	No:	Claims	12-15
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-16
Industrial applicability (IA)	Yes:	Claims	1-16
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Box No. VIII Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

D1= US-A-2 144 612
D2= WO-A-02/50014
D3= JP-A-03 056 430
D4= EP-A-0 781 760
D5= US-A-6 072 076
D6= US-A-2 198 600

SECTION V

1. The present application relates to a process for producing 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol by hydrochlorination of glycerine and/or monochloro-propanediols.

2. The amendments filed with the letter dated 25.06.2005 introduce subject-matter which extends beyond the content of the application as filed, contrary to Article 34(2)(b) PCT. The amendments concerned are the features "vertical cylinder" and "in which there is located a vacuum distillation column downstream of the reactor" of claim 12, "vacuum distillation device" and "located downstream the vacuum distillation column" of claim 13 and "vacuum distillation devices located down-stream the individual steps of the cascade" of claim 14, said features originating from Examples 1-4. However, the apparatuses used in Examples 1-4 include further constructional elements which has been omitted from present claims 12-16. For instance, the apparatus of Examples 1, 3 and 4 uses a disperging device (cf. page 6, line 4, page 7, line 12 and page 8, line 6), a pump (cf. page 6, line 7, page 7, line 15 and page 8, line 12), an evaporator (cf. page 6, line 10, page 7, line 18 and page 8, line 14) and a tank (cf. page 6, line 14, page 7, line 22 and page 8, line 18). The cascade according to Example 2 consists of three reactors (cf. page 6, line 19), wherein the first member of the cascade is a tower reactor of the liquid-gas type (cf. page 6, line 22). It also includes a disperging device (cf. page 6, line 23) and a tank (cf. page 6, line 25). Such generalisation of the spe-cific examples by selecting certain particular features therefrom and incorporating them into broadly defined claims represents an unacceptable extension of the application as originally filed.

For the purpose of the following examination, the aforementioned inadmissible

amendments of claims 12-14 are not taken into account.

3. The process according to present claims 1-11 is novel over the methods known from D1 and D6 by using a solvent-free reaction medium and a distillation under reduced pressure respectively. Thus, the subject-matter of claims 1-11 meets the requirements of Article 33(2) PCT.

4. For claims directed to physical entities such as apparatuses, characteristics of a particular intended use cannot be considered as technical features in determining novelty (cf. PCT Guidelines IV-7.6.). Thus, the expressions "for carrying out the method of any claims 1-9" and "for continuous returning .... as a distillate" used in claim 12, "for continuous returning .... as distillate" of claim 13, and "for carrying out the method of claims 10 or 11" and "for distilling off the water of reaction and a part of the dichloropropanol product" of claim 14 have no limiting effect on the claim´s scope. The apparatuses according to present claims 12-15 are well known from the art (cf. D2, page 7, lines 1-28, Fig. 1; D3, Figures 1 and 2; D4, page 8, lines 1-26, Fig. 1; D5, column 5, lines 4-42, Fig. 1).

   Accordingly, the subject-matter of claim 12-15 lacks novelty, thereby not meeting the requirements of Article 33(2) PCT.

5. The apparatus of claim 16 appears to be novel and satisfies therefore the requirements of Article 33(2) PCT.

6. Documents D1 and D6 cited in the description on page 2, line 25 and page 3, line 1 are considered to represent the closest state of the art. D1 discloses a continu-ous process for the production of glycerol dichlorohydrin which differs from the claimed method in that the reaction is performed in the presence of an inert, wa-ter-immiscible solvent in order to continuously distill out the reaction water (cf D1, page 1, left-hand column, line 48 - right-hand column, line 35, Examples 1-6), and in that the distillation is carried out under atmospheric pressure instead of at redu-ced pressure. Although the practical examples of D1 are focused on the manufac-ture of glycerol dichlorohydrin as a batch process under atmospheric pressure, the document contains unequivocal statements that the reaction may be carried out

under subatmospheric (reduced) pressure (cf. D1, page 3, left-hand column, lines 60-65) and in a continuous manner (cf. D1, page 3, right-hand column, lines 25-48). It is self-evident that the aforementioned continuous distillative removal of the reaction water, an essential feature of the process according to D1, will be maintained in such a continuous mode of operation. The distinction between the claimed process and that of D6 resides in the fact that this document does not mention the possibility of working continuously and distillling at reduced pressure.

7. The problem to be solved by the present application with respect to the cited prior art is to provide a further process for the manufacture of the dichloropropanols 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol. In view of the background art disclosed in D1 and D6 (cf. D1, page 1, left-hand column, lines 19-29, D6, pa-ge 1, left-hand column, lines 17-42) as well as the invention according to D6 (cf. D6, Example 1), it would be obvious for the skilled person to continuously react glycerol with hydrogen chloride in a solvent-free reaction medium and distilling out the water of the reaction, thereby continuously producing a mixture of the dichlo-ropropanol product, water, acetic acid catalyst and hydrogen chloride. Taking into account D1 and common general knowledge, one skilled in the art would also contemplate carrying out the distillation at reduced presure, especially as the ad-vantages thus achieved such as lower distillation temperatures and more effective removal of the reaction water can readily by foreseen. Indeed, the claimed pro-cess does not appear to be associated with any unexpected advantages or surpri-sing effects when compared to the state of the art. According to Example 3 of D1, dichloropropanol is isolated as a pure product with a yield of 91%. In contrast, a mixture of the dichloropropanol product, water and hydrogen chloride is produced by the process of Example 1 of the present invention, the calculated yield of 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol being 95.6%. As disclosed in D1 and D6, dichloropropanol is not conveniently obtainable from these solutions and it is impossible to separate more than a portion thereof by distillation. The only effective methods for producing pure dichloropropanol require that solvent be used, either directly in the reaction mixture (cf. D1) or for extracting the dichloro-propanol product from the distillate (cf. D6). The applicant has failed to provide evidence (comparative experiments) indicating that the claimed process is more effective in terms of yield or other relevant parameters than the method of the art.

For this reason, the subject-matter of claim 1 does not meet the requirements of Article 33(3) PCT.

8. Claims 2-11 and 16 do not appear to contain any features which, in combination with the features of any claim to which they may refer, meet the requirements of the PCT in respect of inventive step. The apparatus of claim 16 can only be acce-pted if the process using this cascade for the production of dichloropropanol is deemed allowable.

SECTION VIII

1. The expressions "etc." (cf. page 4, line 22) and "and the like" (cf. page 5, lines 6, 8 and 18) render the scope of the application unclear (Art. 6 PCT).

2. It would appear that the experiment described in Example 2 does not represent a continuous process (cf. page 6, lines 25-28). Thus, the example extends beyond the scope of claim 1 and should have been denoted as an example not falling within the scope of the invention (Art. 6 PCT).

Amended Claims under PCT Article 34

1. A method of preparing the dichloropropanols 1,3-dichloro-2-propanol and 2,3-dichloro-1-propanol by hydrochlorination of glycerine and/or monochloropropanediols with gaseous hydrogen chloride with catalysis of a carboxylic acid, characterized in that said hydrochlorination is carried out solvent-free in at least one continuous reaction zone at reaction temperatures in the range of 70-140 °C and with continuous removing of the water of reaction by distillation at reduced pressure, the liquid feed containing at least 50 % by weight of glycerine and/or monochloropropanediols.

2. The method according to claim 1, characterized in that the liquid feed contains 80-100 % by weight of glycerine.

3. The method according to claim 1, characterized in that the liquid feed contains, as the monochloropropanediols, 3-chloro-1,2-propanediol and/or 2-chloro-1,3-propanediol.

4. The method according to any of the preceding claims, characterized in that the catalysis is made with acetic acid.

5. The method according to any of the preceding claims, characterized in that the reaction is carried out at a temperature of 100-110 °C.

6. The method according to any of the preceding claims, characterized in that the distillation at reduced pressure is carried out in a rectification zone linked to the reaction zone.

7. The method according to claim 6, characterized in that, together with the removing of the water of reaction by distillation, at least partial primary collection of the product dichloropropanols is made.

8. The method according to claim 6 or 7, characterized in that secondary collection is made, from which dichloropropanols and monochloropropanediols are recycled to the process.

9. The method according to claim 8, characterized in that the secondarily collected residual balance of the reaction mixture is subjected to distillation under reduced pressure in order to separate the higher boiling waste products as the distillation

residue and the dichloropropanols and monochloropropanediols, recycled to the reactor, as the distillate.

10. The method according to any of claims 1-5, characterized in that it is carried out in a cascade of continuous flow reaction zones wherein the water of reaction is collected, together with partial collection of the product dichloropropanols, by distillation at reduced pressure, located always downstream the individual reaction zones of the cascade, and the distillation residue is fed into the next zone of the cascade.

11. The method according to claim 10, characterized in that the reaction mixture exiting from the last step of the cascade is subjected to a two-step distillation, wherein in the first step the water of reaction is separated together with the dichloropropanol reaction product as the distillate and in the second step the higher boiling waste products are separated as the distillation residue and the dichloropropanols and monochloropropanediols are separated as the distillate and are recycled back to the process, preferably into the first step of the cascade.

12. An apparatus for carrying out the method of any of claims 1-9, wherein the apparatus comprises a circulation reactor, consisting of a vertical cylinder, with external circulation, in which there is located a vacuum rectification column downstream of the reactor, for continuous returning the distillation residue from the vacuum rectification column back to the reactor and for continuous collection of a mixture of the dichloropropanol product, the reaction water and the residual hydrogen chloride as a distillate.

13. The apparatus according to claim 12, wherein the apparatus further comprises a vacuum distillation device for continuous removing of the undesired high-boiling waste products as distillation residue and back to the reactor recycled dichloropropanols and monochloropropanediols as distillate, located downstream the vacuum rectification column.

14. An apparatus for carrying out the method of claims 10 or 11, wherein the apparatus comprises a cascade of continuous flow reactors, in which there are vacuum distillation devices located downstream the individual steps of the cascade for distilling off the water of reaction and a part of the dichloropropanol product; the distillation residue being led to the subsequent member of the cascade.

15. The apparatus of claim 14, wherein the number of the members of the cascade is 1 to 5.

16. The apparatus of claim 14 or 15, wherein the number of the members of the cascade is 3.